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maux* from nitrobenzaldehyd, until Wachendorff,† in 1875, described the orthonitrobenzylbromide and chloride. Soon after, in a preliminary notice‡ of a portion of the work contained in these papers, the para- meta- and orthobrombenzylbromides were described; finally, in 1877, Wachendorff published a very interesting paper § upon the nitrobenzylchlorides and bromides, in which he described the metanitrobenzylbromide, and called attention to the striking fact that metanitrobenzylchloride could not be obtained under conditions which gave without difficulty the paranitrobenzylchloride, while he had not as yet succeeded in obtaining the orthonitrobenzylbromide under the conditions which furnished both of its isomeres; he said, however, that he did not despair of obtaining it by new experiments under different conditions; from this it would seem probable that the statements made in his preliminary notice in regard to orthonitrobenzylchloride and bromide, have been proved incorrect by his later experiments.

The object of these papers is to add to our knowledge of this little studied class of compounds, and, also, to make some comparisons between the replaceability of the haloid atoms in the side-chain, which it is hoped may in the future throw some light upon the nature of chemical attraction. The substituted benzylbromides have been used as the starting-point for each class of compounds, because these substances can be easily obtained by the action of weighed amounts of bromine upon the corresponding substituted toluols in the state of vapor. This action of bromine on boiling toluol was first studied by Lauth and Grimaux,|| Cannizaro,¶ and Beilstein,** who proved that the substance thus formed was identical with the benzylbromide previously obtained by Kekule †† from benzylalcohol by means of hydrobromic acid.

FIRST PAPER.

ON CERTAIN SUBSTITUTED BENZYLCHLORIDES.

C. LORING JACKSON.

Parabrombenzylbromide ($C_6H_4Br^P.CH_2Br$). — Preparation. First Method. Ten grammes of pure parabromtoluol, melting-point 28.5° ,

* Grimaux, Comptes Rend., LXV., p. 211; Ann. Chem. Pharm., 145, p. 46.

† Wachendorff, Ber. D. Ch. G., 1875, p. 1101.

‡ Jackson, ib., 1876, p. 931.

§ Wachendorff, Ann. Chem. Pharm., 185, p. 259.

|| Lauth and Grimaux, Bull. Soc. Chim. [2], VII., p. 108.

¶ Cannizaro, Ann. Chem. Pharm., 141, p. 198.

** Beilstein, ib., 143, p. 369.

†† Kekule, Ann. Chem. Pharm., 137, p. 188.

either from the factory of Kahlbaum, in Berlin, or of Schuchardt, in Görlitz, were heated to boiling in a small flask, through whose cork passed a return-cooler and the delivery-tube from a flask containing 10 gr. of bromine, the end of which within the flask was less than a centimeter above the surface of the bromtoluol; the bromine was driven over in the form of vapor by heating the flask containing it with a small flame placed some distance below at such a rate that it was completely decolorized at a few centimeters from the end of the exit-tube: to prevent condensation of the bromine, the delivery-tube was made as short as possible; the heat was carefully regulated so that the bromtoluol boiled gently, the explosive boiling with evolution of white fumes, which was apt to occur toward the end of the process, being especially avoided. If these precautions were observed, the liquid solidified almost completely on cooling, and the substance was easily purified by pressing the crystals thus obtained between filter-paper and recrystallizing once or twice from hot alcohol. The average yield from ten grammes of parabromtoluol was ten grammes of parabrombenzylbromide, that is about sixty-eight per cent of the theoretical amount; but, if more than ten grammes of parabromtoluol were used in one operation, the yield was not so large.

The substance was also obtained from the mixture of para- and orthobromtoluol,* prepared by treating cold toluol with bromine. On cooling the product of the action of bromine on the hot mixture with ice and salt, some parabrombenzylbromide separated out, and more was obtained by distilling off a part of the oil with steam, as the orthobrombenzylbromide distils more easily with steam than the paracompound. This distillation is not to be recommended, however, as under these conditions a portion of the bromide is converted into the corresponding alcohol; but without doubt this difficulty could be removed by using hydrobromic acid in place of water. Compare p. 214.

Second Method. Benzylbromide was treated in the cold with an equal weight of bromine, to which a little iodine had been added; on freezing the product of the reaction, a quantity of parabrombenzylbromide separated out. This method is decidedly inferior to that with pure parabromtoluol, as it not only gives a smaller yield, but also there is a possibility that orthobrombenzylbromide may be formed. The composition of the parabrombenzylbromide was established by the following analyses:—

0.5934 gr. of substance gave 0.7377 gr. CO_2 and 0.1378 gr. H_2O .

* Ann. Chem. Pharm., 147, p. 39.

0.5679 gr. of substance gave, after ignition, with CaO 0.8579 gr. AgBr.

	Required for $C_7H_6Br_2$.	Found.
Carbon	33.6	33.90
Hydrogen	2.4	2.57
Bromine	64.0	64.28
	<hr/> 100.0	<hr/> 100.75

Properties.—Crystallized from alcohol, it forms thick, colorless needles, with a brilliant lustre; from the oily mother-liquor formed in its preparation or from benzole, it separates on slow evaporation in well-formed prisms, apparently of the orthorhombic system, often a centimeter or more long and two to four millimeters thick, which have the consistency of sublimed sal-ammoniac. Its odor is agreeable and aromatic, but its vapor attacks the mucous membrane with very great violence, causing tears and running at the nose; it was observed, however, by all who were exposed continually to its action that they became much less sensitive to it after a few days. When brought upon the more delicate parts of the skin, it causes a sharp, stinging pain, but produces no such effect on the hands; the taste is extremely biting, causing great pain to the tongue for several minutes; it melts at $61\frac{1}{4}^{\circ}$, can be distilled with steam, sublimes in needles, and burns with a luminous green-bordered flame. It is almost insoluble in water, although it imparts its odor to it; (the flat needles, mentioned in a preliminary paper* as separating from water by spontaneous evaporation, were undoubtedly the more soluble parabrombenzylalcohol); it is but slightly soluble in cold, freely in hot alcohol, very readily in ether, benzole, carbonic disulphide, and glacial acetic acid. On one occasion, it was oxidized very rapidly by a mixture of potassic dichromate and dilute sulphuric acid, the action being attended by flashes of light visible even in diffused daylight, the product was an acid melting in the crude state at 239° to 240° , which must therefore be parabrombenzoic acid.

It seems highly probable that this parabrombenzylbromide is the substance obtained, but not purified or studied by Lauth and Grimaux,† in 1866, in the residue from the distillation of bromtoluol; since they described it as crystallizing in needles, and in the highest degree irritating to the eyes.

* Ber. D. Ch. G., 1876, p. 931.

† Lauth and Grimaux, Bull. Soc. Chim. [2], V. p. 347.

Metabrombenzylbromide ($C_6H_4Br.CH_2Br.$ ^m) was made from metabromtoluol, prepared by Wroblevsky's* method (compare also Grete †), as follows: 30 gr. of the mixture of para- and orthoacetoluid, obtained as a secondary product in Wroblevsky's process for purifying orthotoluidin, previously reduced to a granular condition by crystallization from boiling-water, were suspended in cold water, and 45 gr. of bromine dissolved in water added in small portions at a time, shaking until the yellow color disappeared after each addition; the acetyl group was removed from the metabromacetoluid thus obtained by boiling with fuming hydrochloric acid in a flask with a return-cooler; the base, set free by an alkali, was dissolved in portions of 10 gr. at a time in absolute alcohol, and the amido group replaced by hydrogen by Griess's reaction; the alcohol was then partly distilled off on the water-bath; the residue distilled with steam, dried, and rectified, the portion passing over from 179° to 185°, being collected. To convert this into metabrombenzylbromide, 10 gr. of it were heated to boiling, and treated with 12 gr. of bromine in the way described under parabrombenzylbromide (see page 212); the slight excess of bromine over the molecular proportion was taken to allow for the loss in the process; the metabromtoluol took up the bromine somewhat more slowly than the parabromtoluol. The liquid left after the bromining was finished, was distilled in a current of the vapor from hydrobromic acid (boiling-point 125°), prepared according to Naumann,‡ until a considerable portion had passed over: the flask containing the substance was not heated for fear of decomposition. The hydrobromic acid vapor cannot be replaced by steam; as under these conditions some of the brombenzylalcohol might be formed, although I am inclined to think that this reaction would take place much less readily here than it does in the case of the parabrombenzylbromide (compare page 212). The residue left in the flask was transferred to a funnel-tube, closed with a rubber stopper on a glass rod, and surrounded with ice. If the distillation had been carried on long enough, nearly the whole of the oil solidified to a dark, pasty mass. The stopper was then removed, and the brown oil sucked out as completely as possible by means of the Bunsen pump. The white scales left on the funnel were boiled with a small quantity of alcohol; the clear solution poured off from the undissolved oil and cooled in a corked flask. As soon as no more oil was

* Wroblevsky, Ann. Chem. Pharm., 168, p. 153.

† Grete, ib., 177, p. 231.

‡ Naumann, Ber. D. Ch. G., 1876, p. 1574.

deposited, the clear liquid was decanted into another flask, and cooled with ice, when crystals were formed. The same process was repeated with the mother-liquor and the residue until the whole was converted into crystals; while another crop of less pure metabrombenzylbromide was obtained by adding snow to the mother-liquor from the final operation. The crystals were purified by similar crystallizations from hot alcohol. It was necessary that all these operations should be carried on in corked flasks, as the metabrombenzylbromide, when moistened with alcohol, evaporated when exposed to the air so rapidly that there was a very considerable loss from working with open vessels.

The composition of the metabrombenzylbromide was established by the following analyses:—

0.4333 gr. substance gave after ignition with CaO 0.6609 gr. AgBr.

	Required for $C_7H_6Br_2$.	Found.
Carbon	33.6	34.63
Hydrogen	2.4	2.66
Bromine	64.0	63.96
	<hr/> 100.0	<hr/> 101.25

Properties.—Crystallized from alcohol by cooling, it forms white bladed needles or plates arranged in radiated groups; by slow evaporation of its alcoholic solution, it can be obtained in flat prisms with square ends sometimes reaching a length of 3 cm., and a breadth of 2 mm. It has an agreeable odor, aromatic, but different from that of the parabrombenzylbromide, while its action on the mucous membrane is even more violent, perhaps because it is more volatile; its taste and action on the more delicate parts of the skin is similar to that of the para compound; it melts at 41° , can be distilled with steam only very slowly, sublimes in oily drops, and burns with a luminous flame having a green border. One of its most striking properties is that, when moistened with alcohol or ether, it evaporates very rapidly; whereas when dry it is comparatively fixed. It is almost insoluble in water, but imparts its odor to it, is freely soluble in cold, still more so in hot alcohol, and very readily soluble in ether, benzole, carbonic disulphide, and glacial acetic acid. An oxidizing mixture of potassic dichromate and dilute sulphuric acid seems to be without action on it; but the same mixture converts the alcohol derived from it into an acid, which, in a not perfectly pure state, melts at 151° , and must therefore be metabrombenzoic acid.

Orthobrombenzylbromide ($C_6H_4Br.CH_2Br$).—After several unsuccessful attempts to obtain an orthobromtoluol free from the para com-

pound from the mixture prepared by adding bromine to cooled toluol, I decided to insure a perfectly pure substance as my starting-point, by making the orthobromtoluol from orthotoluidin. The first method employed for purifying the orthotoluidin was that of Wroblevsky,* by boiling crude toluidin sixteen hours with glacial acetic acid; but all the samples obtained by this process contained traces of paratoluidin. After I had convinced myself by experiment that the methods of Rosenstiehl,† by treating the oxalates with ether; and of Beilstein and Kuhlberg,‡ by precipitating an acetic acid solution of acetoluid with water, — were almost impracticable for large quantities, I tried the method of Schad,§ recommended by Kekule,|| which depends on the crystallization of the nitrates and chlorides, and in this way succeeded in obtaining a liquid toluidin which with acetylchloride gave an acetoluid melting after one recrystallization from boiling-water at 107°. As some previous attempts to convert orthotoluidin into orthobromtoluol by the usual method through the diazoperbromide had given me as unsatisfactory a yield as that obtained by Wroblevsky,¶ I treated this according to a new modification of the process of Hübner and Majert** for preparing parachlortoluol, which I had found to work admirably in making that substance. This modification was suggested by Victor Meyer's †† method of applying Griess's reaction, and consisted in dissolving 20 gr. of the orthotoluidin in an excess of hydrobromic acid (boiling-point 125°, prepared according to Naumann ‡‡); the pasty mass was then treated with somewhat more than the calculated amount of solid potassic nitrite, which was thrown in in small portions at a time, the flask being corked after each addition, and shaken until all the red fumes were absorbed; after the last portion of nitrite had been added, the greater part of the liquid was distilled off, and the residue then treated again in the same way. The distillate consisted of dilute hydrobromic acid and a heavy oily liquid which was separated with a drop-funnel, washed with potassic hydrate solution until the odor of kresole was removed, then with water, and finally dried and rectified; in this way 40 grammes of orthotoluidin gave 29 grammes of crude

* Wroblevsky, *Ann. Chem. Pharm.*, 168, p. 162.

† Rosenstiehl, *Zeitschr. Chem.*, 1868, p. 557, 666.

‡ Beilstein, *Ann. Chem. Pharm.*, 156, p. 75.

§ Schad, *Ber. D. Ch. G.*, 1873, p. 1361.

|| Kekule, *Ber. D. Ch. G.*, 1874, p. 1006.

¶ Wroblevsky, *Ann. Chem. Pharm.*, 168, p. 171.

** Hübner and Majert, *Ber. D. Ch. G.*, 1873, p. 794.

†† V. Meyer, *Ber. D. Ch. G.*, 1875, p. 1074, note.

‡‡ Naumann, *Ber. D. Ch. G.*, 1876, p. 1574.

orthobromtoluol, and 24 grammes of this gave on the first fractioning 19 grammes of a colorless liquid boiling between 179° and 182° ; that is, about thirty-six per cent of the theoretical yield, whereas the diazoperbromide furnishes under the best conditions only ten per cent. The new method has the further advantages of taking much less than half the time occupied by either of the old ones, and the product is not contaminated with the nitro compounds which compelled Hübner and Majert to reduce before rectifying. Von Richter * has also obtained tetrabrombenzole by the action of nitrous anhydride on a mixture of tribromaniline with hydrobromic and glacial acetic acids; he ascribes the reaction to the presence of the negative atoms, and announces his intention of trying similar experiments with compounds containing fewer bromine atoms or nitro groups; that the reaction is not due to the presence of such negative radicals is proved by the previous researches of Hübner and Majert, which he seems to have overlooked, and the results given above. I should not have intruded on Von Richter's field of work, had it not been necessary for me to obtain the orthobromtoluol, but I felt the less hesitation in doing so, as I am unable to see that his method differs in any essential particular from that of Hübner and Majert, published nearly two years before the appearance of his article.

The orthobromtoluol was converted into orthobrombenzylbromide by treatment with bromine in the way described under the para compound. The purification of the substance was a matter of some difficulty, as it seemed to be completely decomposed by rectification, and converted into the alcohol by distillation with steam; the method finally adopted was distillation in a stream of the vapor from aqueous hydrobromic acid, as described under the metabrombenzylbromide; the first fifth of the distillate was rejected to make sure of the absence of orthobromtoluol; that which came over later was washed till it ceased to give an acid reaction, and then dried *in vacuo*. In this way, 17 grains of pure orthobrombenzylbromide were obtained from 18 grains of orthobromtoluol.

Its purity was established by the following bromine determination:—

0.5035 gr. of substance gave after ignition with CaO 0.7608 gr. of AgBr.

	Required for $C_7H_5Br_2$.	Found.
Bromine	64.0	64.30

* Von Richter, Ber. D. Ch. G., 1875, p. 1428.

A number of bromine determinations made in products from distillation with steam gave invariably results which were below the theory.

Properties.—It forms a pale yellow oil (the color is undoubtedly due to a trace of some impurity), with an agreeable odor, somewhat resembling that of parabrombenzylbromide, and an action on the mucous membrane even more violent than that of the preceding compounds; its boiling-point seems to lie between 250° and 260° , but could not be determined with accuracy because it is decomposed with evolution of hydrobromic acid by boiling. A careful study of the action of heat on this and the allied substances is reserved for a future paper. It does not solidify even at -15° , can be distilled with steam, burns with the usual luminous green-bordered flame, and does not mix with water, although it imparts its odor to it, but mixes readily with absolute alcohol, ether, benzole, glacial acetic acid, and carbonic disulphide. It does not seem to be attacked by a mixture of potassic dichromate and dilute sulphuric acid, but the alcohol derived from it is completely destroyed by this oxidizing mixture.

Parachlorbenzylbromide, $C_6H_4ClCH_2Br$, was prepared from parachlortoluol; melting-point, $6^{\circ}.5$; boiling-point, 158° – 161° ; made by the modification of the method of Hübner and Majert, already described in connection with orthobromtoluol (see page 216); crude fuming hydrochloric acid took the place of the hydrobromic acid, and 40 gr. of paratoluidin were used for each operation; the oil, after washing with potassic hydrate, proved on rectification to be almost absolutely pure parachlortoluol, the yield being about 13 gr. It was converted into parachlorbenzylbromide in the way already described; the product of the reaction deposited crystals on cooling, which were drained, and a fresh crop obtained from the mother-liquor by heating it gently for a few minutes in a watch-glass placed on a sand-bath, and then allowing it to stand for some time. The crystals after pressing between filter-paper were purified by crystallization from hot alcohol in corked flasks, as the substance is so volatile that work in open vessels would have been attended with great loss; upon cooling the solution with ice, a little oil separated; and if the liquid was then stirred it immediately became filled with beautiful white needles. On one occasion, the substance was distilled with steam in order to obtain it perfectly white, but this is not to be recommended, as the water left in the distillation-flask deposited long thin ribbons melting at 66° , and therefore evidently the parachlorbenzylalcohol, while the supernatant liquid contained hydrobromic acid. This

observation furnished a very neat and convenient way of obtaining the corresponding alcohols from the bromides. (See parabrombenzylalcohol in the next paper, p. 221).

The composition of the parachlorbenzylbromide was established by the following analyses:—

0.3399 gr. of the substance gave after ignition with CaO 0.5580 gr. AgBr+AgCl.

0.4224 gr. of substance gave 0.6779 gr. AgBr+AgCl.

	Required for C_7H_6Cl Br.	Found.
Chlorine and Bromine	56.20	57.20
		55.94

Properties.—By slow evaporation of its alcoholic solution, it can be obtained in well-formed colorless prisms, by cooling in radiated bunches of needles often three centimeters long; it has an agreeable aromatic odor, and acts on the mucous membrane more violently than any of the other substances described in this paper; it melts at $48\frac{1}{2}^\circ$, sublimes in oily drops, can be distilled with steam, is very volatile at ordinary temperatures, so that a crystal will evaporate completely if exposed to the air for a few days, and burns with a flame similar to that of the bromine compounds. It is slightly soluble in water, easily soluble in cold, still more so in hot alcohol, and very readily in ether, benzole, carbonic disulphide, and glacial acetic acid. It is attacked with difficulty, if at all, by potassic dichromate and dilute sulphuric acid.

Paraiodbenzylbromide, $C_6H_4ICH_2Br$, was made from paraiodtoluol; melting-point, 35° ; prepared according to Körner* by the action of hydriodic acid on the nitrate of diazotoluol, this last being obtained by Victor Meyer's† excellent modification of Griess's reaction. The introduction of the bromine into the side-chain by treating the boiling substance with bromine vapor was much more difficult than in the preceding cases; the precautions to be observed were in general the same as those given under parabrombenzylbromide; but occasionally, in spite of all possible care, a black tarry liquid was the only result of the process. The conditions under which the paraiodbenzylbromide is formed are now undergoing very careful study by Mr. C. F. Mabery, and the results will be published in his paper upon the paraiodbenzyl compounds. It is a very remarkable fact that in several cases, when the paraiodtoluol was not perfectly pure, the liberation of iodine in considerable quantity was observed during the bromining; but, in spite of this, the product contained paraiodbenzylbromide, thus apparently

* Körner, Bull. Acad. Roy. Belg. [2], 24, p. 157.

† V. Meyer, Ber. D. Ch. G., 1875, p. 1074, note.

furnishing an exception to the general rule of Beilstein that, in presence of iodine, bromine goes into the benzole ring even at high temperatures. The product of the reaction, if properly managed, solidified on cooling, and was best purified by standing on paper, which sucked out a quantity of black oil, and afterward by repeated crystallizations from boiling alcohol with the assistance of bone-black.

The composition of the paraiodbenzylbromide was determined by the following analyses:—

0.3721 gr. of substance yielded 0.3773 gr. CO_2 and 0.0773 gr. of H_2O .
 0.1774 gr. of substance gave, according to Carius, 0.1285 gr. of Ag.
 0.1971 gr. of substance gave 0.2755 gr. of $\text{AgBr} + \text{AgI}$. There were indications in this analysis that the oxidation had not been complete.

	Required for $\text{C}_7\text{H}_5\text{IBr}$.	Found.	
Carbon	28.28	27.66	
Hydrogen	2.03	2.31	
Iodine and Bromine	69.69	69.47	68.41
	<hr/> 100.00	<hr/> 99.44	

Properties.—Crystallized from alcohol, it forms flattened needles, which usually have a straw yellow color, but can be obtained white by repeated recrystallization with boneblack. It has an aromatic odor and attacks the mucous membrane much less violently than any of the other substances mentioned in this paper; this, however, is very probably due to the fact that it is not readily volatile at ordinary temperatures; it melts at $78\frac{3}{4}^\circ$; does not distil with steam or only with great difficulty; sublimes in needles; burns with a luminous green-bordered flame; and is insoluble in water, almost so in cold, much more soluble in hot, alcohol, but slightly soluble in glacial acetic acid, freely in ether, benzole, and carbonic disulphide. It is not easily attacked if at all by an oxidizing mixture of potassic dichromate and dilute sulphuric acid.

That all the substances mentioned in this paper contain bromine in the side-chain is proved by the fact that, when boiled with alcoholic sodic acetate, each one of them yields the corresponding substituted benzylacetate, from which the alcohol can be obtained by heating with aqueous ammonia at 150° to 160° . The description of these compounds, as well as of certain other derivatives of these substances, will be found in the following articles of this series. For descriptions of the parachlorbenzyl compounds the reader is referred to the papers already cited in the introduction.